Effect of Outside Air Ventilation Rate on Volatile Organic Compound Concentrations in a Call Center

A.T. HODGSON[*], D. FAULKNER, D.P. SULLIVAN, D.L. DIBARTOLOMEO,
   M.L. RUSSELL, and W.J. FISK

Indoor Environment Dept., Environmental Energy Technologies Division, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Abstract

A study of the relationship between outside air ventilation rate and concentrations of volatile organic compounds (VOCs) generated indoors was conducted in a call center office building. The building, with two floors and a total floor area of 4,600 m^2, is located in the San Francisco Bay Area, CA. Ventilation rates were manipulated with the building's four air handling units (AHUs). VOC and CO_2 concentrations in the AHU returns were measured on seven days during a 13-week period. VOC emission factors were determined for individual zones on days when they were operating at near steady-state conditions. The emission factor data were subjected to principal component (PC) analysis to identify groups of co-varying compounds. Potential sources of the PC vectors were ascribed based on information from the literature. The per occupant CO_2 generation rates were 0.0068-0.0092 L s^{-1}. The per occupant isoprene generation rates of 0.2-0.3 mg h^{-1} were consistent with the value predicted by mass balance from breath concentration and exhalation rate. The relationships between indoor minus outdoor VOC concentrations and ventilation rate were qualitatively examined for eight VOCs. Of these, acetaldehyde and hexanal, which likely were associated with material sources, and decamethylcyclopentasiloxane, associated with personal care products, exhibited general trends of higher concentrations at lower ventilation rates. For other compounds, a clear inverse relationship between VOC concentrations and ventilation was not observed. The net

[*] Corresponding author, Ph. 510-486-5301, Fax 510-486-7303, E-mail ATHodgson@lbl.gov

concentration of 2,2,4-trimethyl-1,3-pentanediol monoisobutryate isomers, an example of a low volatility compound, changed very little with ventilation likely due to sorption and re-emission effects. These results illustrate that the efficacy of ventilation for controlling VOC concentrations can vary considerably depending upon the operation of the building, the pollutant sources and the physical and chemical processes affecting the pollutants. Thus, source control measures, in addition to adequate ventilation, are required to limit concentrations of VOCs in office buildings.

Key word index: Indoor air quality, Office building, VOC emission rates, Formaldehyde, Principal component analysis

Introduction

Ventilation defined as the delivery of outdoor air (OA) to occupied spaces occurs in most large commercial buildings through integrated mechanical systems, also providing heating and cooling. Contributions of infiltration of OA through the building envelope are relatively small. In office buildings, mechanical systems are designed to provide a specific flow rate of OA per occupant or per floor area. The importance of providing adequate ventilation in office buildings is supported by studies, reviewed and assessed by Seppänen *et al*. (1999), that have investigated the association of ventilation rates or carbon dioxide concentrations with occupant responses. The human outcomes typically were the prevalence of sick building syndrome symptoms or perceived air quality problems ascertained by self-administered questionnaires. Many of the studies found that ventilation rates below 10 L s^{-1} per person were associated with one or more adverse outcomes. Ventilation rate increases above this rate were found in some studies to decrease symptom prevalence or improve perceptions. Since ventilation does not directly affect occupant health or perception, the associations were presumably due to improvements in environmental conditions such as reductions in the concentrations of airborne gas- and particle-phase contaminants (*ibid*.). Among these, considerable attention has been directed toward

2

volatile organic compounds (VOCs), which have numerous indoor sources and the potential to affect health and comfort. This important contaminant class is the focus of this paper.

Despite a general association of occupant health and satisfaction with increased ventilation, the effectiveness of ventilation for controlling concentrations of gas-phase pollutants in office buildings remains an open question. In well-mixed spaces operating at constant conditions with respect to ventilation and pollutant parameters, the concentrations of gas-phase pollutants from indoor sources are inversely related to ventilation by steady-state mass-balance considerations. However, ideal steady-state conditions rarely prevail in occupied buildings. In addition, the relationship between ventilation and gas-phase concentrations likely is complicated by other building- and pollutant-related factors. The importance of such factors was addressed by the current study, which investigated how the concentrations of VOCs generated indoors in a single office building were affected by manipulated changes in ventilation rate. This study was performed in conjunction with an investigation of the effects of ventilation rate on the productivity of call center workers (Fisk *et al.*, 2002).

Methods

The study was conducted in a health maintenance organization call center located in the San Francisco Bay Area, CA. The building, constructed in 1998, has two floors and a total floor area of 4,600 m^2. It has sealed windows and a mechanical ventilation system with air conditioning. Floors are carpeted, ceilings are open, and smoking is not allowed. The building is divided into four interior zones ranging in size from 840 to 1,460 m^2. Each zone is served by a roof-mounted, variable air volume, air handling unit (AHU) that modulates the supply rates of cool or warm air to maintain indoor temperatures in the desired range. Corridors and doorways separate the interior zones. Doors are usually left open to allow mixing between adjacent zones. One AHU (2-2) serves the entryway, staff lounge, and offices for management staff and meetings. The other AHUs serve the three zones occupied by advice registered nurses (RNs) and telecommunications service representatives (TSRs). The numbers of RNs and TSRs logged into

work was determined in half-hour increments. There are ~40 administrators and support staff. The workforce is predominantly female. The total occupant density during the study was approximately five persons per 100 m^2, although the building is designed for higher occupancy.

Each AHU has an economizer control system. Equipment was added to enable automatic manipulation and measurement of OA ventilation rates (Fisk *et al*. 2002). AHU supply flow rates were measured using arrays of pitot tubes in supply ducts, with pressure differences logged. A single CO_2 monitor, calibrated weekly with multi-level gas standards, measured concentrations of CO_2 on a 7.2 minute cycle in OA, the return air streams, and the supply air streams. The fraction of outside air (FOA) in each AHU was calculated by simple mass balance from the CO_2 data as FOA = (Supply – OA)/(Return – OA) for periods in which FOA was not less than zero. The OA flow rate in each AHU was then computed as the product of the supply airflow rate and FOA.

The dampers in AHU 2-2 were fixed in one position. For the three AHUs serving zones occupied by RNs and TSRs (1-1, 2-1 and 2-3), three fixed damper positions were selected to provide periods of low, medium, and high ventilation rates. The damper positions for the low period were set at positions intended to provide near the code-minimum OA supply rate of 76 L s^{-1}/100 m^2. The damper positions for medium and high periods were set to provide approximately 2- and 4-times the code minimum. In a fourth ventilation setting, the normal control systems for the OA supplies, including the outside air economizers, were activated. Using these methods, periods of ventilation were scheduled over 13 weeks (July 28 through October 24, 2000) in one of four modes: low, medium, high, and economizer mode. In weeks 3-6, 9 and 10, the rates were randomized and changed daily.

Sampling for VOCs and aldehydes was conducted on weeks 2, 3, 6-8, 11 and 13. Air samples were collected simultaneously from the return air ducts of the four AHUs and OA on Tuesdays. OA samples were collected ~0.6 m above the roof underneath an elevated supply duct. Sampling began at 10:00 and ended at 15:00 to encompass the period of maximum occupancy.

4

Air samples for VOCs were collected on Tenax-TA™ sorbent tubes (P/N CP-16251; Varian Inc.) modified by substituting a 15-mm section of Carbosieve S-III 60/80 mesh (P/N 10184, Supelco Inc.) at the outlet end. Air was pulled through the sorbent tubes using peristaltic pumps actuated by timers. Pump flow rates, measured near the beginning and end of each sampling period, were ~5 mL min^{-1} yielding sample volumes of ~1.5 L. Each sample was collected in duplicate. Field blanks were obtained weekly. These samples were quantitatively analyzed for individual VOCs by thermal desorption-gas chromatography/mass spectrometry (U.S. EPA, 1984). Samples were thermally desorbed and concentrated on a cryogenic inletting system (Model CP-4020 TCT; Varian Inc.). Desorption temperature was set to 235 °C for 6.5 min. The cryogenic trap was held at -100 °C and then heated to 235 °C for injection. Multi-point calibrations were referenced to 1-bromo-4-fluorobenzene as an internal standard. There were 62 target compounds spanning broad ranges of volatility and chemical functionality.

Air samples for formaldehyde and acetaldehyde were collected onto treated silica-gel cartridges (P/N WAT047205, Waters Corp.) using separate peristaltic pumps. Sampling flow rates were ~150 mL min^{-1} yielding sample volumes of ~45 L. Each cartridge was extracted with 2 mL of acetonitrile. Extracts were analyzed by high-performance liquid chromatography with a diode array detector at a wavelength of 365 nm (ASTM, 1997a). Extract concentrations were determined from multi-point calibrations of external standard mixtures.

Concentrations of individual VOCs and aldehydes (ppb; 298° K, 101 kPa) and CO_2 (ppm), averaged over the 5-h sampling interval, were determined for OA and the return air of the four AHUs on each day of sampling. Emission rates (μg h^{-1}) were derived by the steady-state form of the mass-balance model for continuously stirred tank reactors (ASTM, 1997b):

$$ER = Q\,(C - C_0) \tag{1}$$

Where Q is the flow rate in an AHU (m^3 h^{-1}) and $C - C_0$ is the indoor minus outdoor concentration (μg m^3). Losses of compounds due to factors other than ventilation (*e.g.*, as the result of irreversible sink effects or chemical reactions in air) were ignored; thus, the computed

values are net rates. Emission factors (μg m^{-2} h^{-1}) were calculated by normalizing the emission rates to the floor areas of the respective zones. Seven of the 28 samples were excluded from this analysis because the interval between the change in airflow rate and the initiation of sampling was insufficiently long to establish near steady-state conditions.

The emission factors of predominant, indoor-derived VOCs in samples collected at steady state were analyzed by principal component (PC) analysis as a means to categorize and identify emission sources. PC analysis is a multivariate statistical tool for reducing the dimensionality of a data set consisting of a number of interrelated variables. The technique converts highly correlated variables to a reduced number of uncorrelated vectors, which are linearized sums (PCs) of standardized individual variables (*i.e.*, normalized to mean = 0 and standard deviation = 1). It is hypothesized that correlated compounds will tend to group on a single PC because they have common or closely linked emission sources. Compounds originating from more than one source will be associated with more than one PC. The software was StatView for Windows (Ver. 5.0.1, SAS Institute Inc.). A cutoff criterion for correlation matrix eigenvalues of ≥ 1.0 was used to determine which PCs were kept in the analysis. The varimax rotation method was employed.

Results

The total OA flow rate for the building ranged from 19,100 to 48,6000 m^3 h^{-1}, a 2.5-fold difference, over the seven sampling days (Table 1). This was equivalent to a building average air exchange rate range of 1.35 to 3.4 h^{-1}. The numbers of RNs and TSRs logged into work were highest in the morning hours and typically declined towards the ends of the sampling intervals. Variations in occupancy between 8:00 and 15:00 typically were about 25% or less. The average numbers of RNs, TSRs and an assumed 40 administrative and support staff who were present in the building during the 8:00-15:00 interval ranged from 211 to 273 over the seven sampling days (Table 1). There were approximately ten fewer RNs and TSRs averaged over the 5-h sampling interval on each day.

Normalized airflow rates (L s^{-1}/100 m^2) for each of the AHU zone on the seven sampling days are presented in Fig. 1. By design, AHU 2-2 flow rates remained relatively constant (<25% variation). There were approximate 5-, 7- and 3-fold variations over the seven days between the low and high rates in AHUs 1-1, 2-1 and 2-3, respectively. The ventilation conditions in these three zone on the sampling days of weeks 8 and 13 were intended to approximate the code-minimum OA supply rate of 76 L s^{-1}/100 m^2. Conditions on the sampling days in weeks 3 and 7 were intended to be twice the minimum OA supply rate, but AHU 2-1 was operating at the lowest setting in week 3. Conditions on the sampling days in weeks 2, 6 and 11 were intended to be four times the minimum, but generally fell short of this goal.

About ten of the target VOCs were not detected in any samples and a number of other compounds, including chlorinated hydrocarbon solvents, occurred at very low concentrations. The 21 VOCs with geometric mean indoor concentrations of ~0.2 ppb or higher and indoor/outdoor concentration ratios predominantly above unity are listed in Table 2. They are ordered in this and the subsequent table by chemical class (*i.e.*, alcohols, ketones, aldehydes, esters, aromatic hydrocarbons, terpene hydrocarbons and misc.) and then by decreasing volatility within class. Indoor and outdoor concentrations and indoor/outdoor concentration ratios are summarized as geometric means and ranges. VOC concentrations less than lower limits of quantitation (based on a 0.5-2 ng compound-dependent instrumental limit) were averaged as one half the quantitation limit. Indoor geometric mean VOC concentrations were below 5 ppb, with the exceptions of ethanol, isopropanol, acetone, and formaldehyde. Outdoor geometric mean concentrations were below 1 ppb, with the exceptions of the same compounds plus acetaldehyde. For approximately half the reported VOCs, concentrations in the majority of outdoor samples were below quantitation limits.

In-Out concentrations of eight selected VOCs are plotted in Fig. 2 versus normalized airflow rate (L s^{-1}/100 m^2). Only steady state data are included in the plots. These compounds were chosen to span a broad volatility range from very volatile compounds (*e.g.*, formaldehyde, acetaldehyde and isopropanol), with low sorption rates on surfaces, through lower volatility

compounds (*e.g.*, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate combined isomers or TMPD-MIB) with substantially higher sorption rates on surfaces.

Whole building net emission factors for the week 2, 6, 7 and 13 sampling days in which all samples were collected near steady-state conditions were calculated as the sums of the zonal emission rates divided by the total building area. Emission factors for 20 VOCs in $\mu g\ m^{-2}\ h^{-1}$ and CO_2 in $g\ m^{-2}\ h^{-1}$ are presented in Table 3. m/p-Xylene was excluded because more than one-half of its In-Out concentrations were below the limit of quantitation. The sums of the VOC emission factors on the four sampling days ranged from 1.65 to 2.7 $mg\ m^{-2}\ h^{-1}$. Much of this mass was accounted for by a few compounds including ethanol, isopropanol, acetone, decamethylcyclopentasiloxane (d5 siloxane) and, in some weeks, 2-butoxyethanol.

Zonal average emission factors were calculated as the averages of the 21 zonal measurements made near steady-state conditions. These are summarized in Table 3 as geometric mean concentrations and ranges. The individually measured CO_2 emission factors, which varied 2.3-fold, exhibited the least variability by time and zone. VOCs which varied ~5-fold or less by time and zone, included ethanol, acetaldehyde, hexanal, isoprene, α-pinene, and d5 siloxane. Isopropanol, 2-butoxyethanol, methyl isobutyl ketone (MIBK), ethyl acetate and butyl acetate exhibited the most variability with a 25-fold or more difference between minimum and maximum values.

The results of the PC analysis of the emission factors for 16 predominant VOCs measured in the 21 samples collected at steady state are presented in Table 4. CO_2, which is solely produced from breath, was included in the analysis as an indicator of occupant-related sources. Ethanol, an abundant compound, was excluded because of the relatively high uncertainty in its measurement. The first five rotated PCs of the analysis of VOC and CO_2 emission factors accounted for 83% of the total variance. Coefficients between 0.29 and -0.29 have been omitted from the table to improve readability and facilitate the identification of sources.

Discussion

The composition and concentrations of VOCs in the study building were generally consistent with data reported in the literature for North American office buildings studied since 1990 (Daisey *et al*., 1994, Girman *et al*., 1999, Shields *et al*., 1996). Oxygenated solvents such as ethanol, isopropanol, acetone and 2-butoxyethanol often dominate the mixtures in office buildings. A notable difference for the study building is the virtual absence of chlorinated hydrocarbon solvents. This may, in part, reflect reductions over recent years in the production and use of environmentally harmful and toxic halocarbons.

Through our selection process, most the VOCs listed in Table 2 predominantly derive from indoor sources in this building. Assuming a typical measurement precision of 25% for individual VOCs, the uncertainty in the indoor/outdoor ratio for a compound derived entirely from outdoors is about 1 ± 0.35 by propagation of uncertainty (*i.e.*, square root of the sum of the squares of the two measurement precisions). Thus, indoor/outdoor ratios below 1.35 are indicative of an outdoor source. Two compounds, toluene and m/p-xylene have geometric mean indoor/outdoor ratios near this value indicating they have strong outdoor source contributions, likely motor vehicle emissions (Daisey *et al*., 1994). Indoor concentrations of acetaldehyde and heptanal also are strongly influenced by outdoor sources.

Occupants were the likely exclusive source of CO_2 in the building. The per occupant CO_2 generation rates calculated for the sampling days when the building was at near steady-state conditions are in the range of 0.0068-0.0092 L s^{-1} (Table 5). These values are elevated over a generation rate of 0.0052 L s^{-1} calculated for an average-sized adult engaged in office work but within the upper bound of 0.010 L s^{-1} for office workers (Persily, 1997).

Principal component analysis previously has been applied to VOC concentrations measured in cross-sectional studies of office buildings and residences in attempts to ascertain sources (Apte and Daisey, 1999; Apte and Erdmann, 2002; Edward *et al*., 2001; Ten Brinke *et al*., 1998). It was anticipated that PC analysis of emission factors in a single building might produce more specific source information. In fact, the loadings of the predominant indoor-derived VOCs on

9

the PC vectors demonstrated that the emission factors of many compounds were interrelated (Table 4). In many cases, the observed groupings likely were due to commonalties among the emission sources. However, there were inconsistencies that are difficult to explain based on the known sources of some compounds. Because all samples were collected during normal business hours with similar occupancy, the analysis may not separate some occupant-generated sources from building-related sources. Furthermore, differences in the physical and chemical behaviors of compounds in a building serve to obscure associations based on source similarities. With these limitations in mind, the following tentative source identifications were made based on the groups of highly correlated VOCs and on available information from the literature supporting the indicated associations.

PC1, with high loadings of 2-ethyl-1-hexanol, TMPD-MIB, formaldehyde, CO_2 and d5 siloxane, is difficult to rationalize. Occupant-related sources are implied, as CO_2 is a direct indicator of occupancy. The d5 siloxane is used as a major ingredient in personal deodorants and previously has been associated with occupancy in office buildings (Shields *et al*., 1996). If all of the d5 siloxane is attributed to this source, the average per occupant generation rates are in the range of ~3-6 mg h^{-1} (Table 5). Unexplainably, isoprene, which is a predominant VOC in breath (Fenske and Paulson, 1999), has a weak negative correlation with PC1 (loading = -0.19). Occupant sources may contribute, in part, to the other compounds with high loadings on PC1, but building sources more likely predominate. TMPD-MIB is used as a coalescing aid in latex paints and emissions of TMPD-MID from wallboard continues over a number of months after paint application (Hodgson, 1999). TMPD-MIB also is used in cosmetic nail care products (Eastman Chemical Co., 2003), providing a possible link to occupants as a source. Formaldehyde can derive from many sources potentially present in office buildings including composite wood products, architectural finishes, thermal and acoustical insulation, fabrics and paper (Kelly *et al*., 1999). In addition, formaldehyde is present in nail care products (*ibid*.) and in some cosmetic lotions and shampoos (Rastogi, 1992). Thus, an occupant association might occur due to formaldehyde emissions from workstation components, office supplies, clothing or

10

cosmetics. 2-Ethyl-1-hexanol is an industrial solvent with numerous uses and can be produced by hydrolysis of diethylhexyl phthalate; a link with occupancy has not been documented to our knowledge.

With the exceptions of CO_2, d5 siloxane and 1-butanol, the compounds associated with PC1 share the characteristic that their emission factors were elevated at the higher ventilation rate conditions (Table 3). TMPD-MIB, 2-ethyl-1-hexanol and possibly d5 siloxane are sorbed to surfaces in a manner consistent with their saturation vapor pressures. Their emission factors then are dependent upon changes in the gas-phase concentration relative to the sorbed surface concentration. Gas-phase formaldehyde, which is very water soluble, may be in equilibrium with formaldehyde dissolved in aqueous surface films making its emission rate also dependent upon ventilation.

PC2, with high loadings of MIBK, butyl acetate, acetaldehyde, pentanal, and hexanal, possibly is indicative of a material source, such as furnishings. A similar compound association was produced as the first PC in an analysis of the concentrations of 19 VOCs measured in 41 U.S. office buildings (Apte and Erdmann, 2002). Acetaldehyde, pentanal, and hexanal are all emitted by composite wood products (Hodgson *et al*., 2002). However, wood products typically emit hexanal at much higher rates than acetaldehyde rather than the similar rates seen here. A possible source of MIBK and butyl acetate is furniture coatings (Salthammer, 1997). The negative correlation of formaldehyde with PC2 indicates that the sources of formaldehyde and the other aldehydes are different.

PC3, with high loadings of acetone, isopropanol, 2-butoxyethanol, and 1-butanol, possibly represents the emissions of solvents from cleaning solutions. A PC analysis of VOC concentrations in 12 California office buildings produced a similar high correlation between isopropanol and 2-butoxyethanol (Ten Brinke *et al*., 1998). Commonly used glass and surface cleaners and some general-purpose cleaners contain 2-butoxyethanol but not necessarily acetone or isopropanol (Zhu *et al*., 2001). In addition, products in these same categories frequently

contain d-limonene (*ibid*.). These observations suggest that PC3 may be indicative of solutions used to clean office equipment for which we were unable to find published data.

PC4, with high loadings of d5 siloxane, toluene, and isoprene, is likely associated with occupants. This is indicated by multiple factors. CO_2 is a secondary contributor. The d-5 siloxane has a documented occupant source. The isoprene concentrations in the building are consistent with an occupant source. The per occupant isoprene generation rates calculated for the sampling days when the building was operating at near steady-state conditions, are in the range of ~0.2-0.3 mg h^{-1} (Table 5). These values are consistent with an adult isoprene generation rate of 0.27 mg h^{-1} predicted using breath concentration and exhalation rate (Fenske and Paulson, 1999). Finally, toluene is a major constituent of some nail enamel removers (Zhu *et al*., 2001).

d-Limonene, which is the sole highly loaded compound on PC5, is used in air fresheners and as an odorant and active ingredient in cleaning products (*ibid*.). The occupant related compounds CO_2 and d5 siloxane are secondary contributors. In a Nordic study, PC analysis of VOC concentrations in smoke-free workplace environments also produced a vector dominated solely by d-limonene (Edwards *et al*., 2001). Air fresheners, cleaning products and personal fragrances were indicated as the likely sources.

The ability of ventilation to control the concentrations of a range of air pollutants deriving from different sources was examined qualitatively. In-Out concentrations were used in this assessment in order to focus solely on pollutant sources associated with the building and occupants. The eight VOCs plotted versus normalized airflow rate in Fig. 2 were variously identified with different source categories. The concentrations of isopropanol and 2-butoxyethanol, two compounds with cleaning product sources (PC3), showed little relationship with ventilation; however, the two highest isopropanol values occurred at the lowest airflow rates. Formaldehyde concentrations with numerous potential sources also were apparently unassociated with ventilation as the concentrations in the zones served by AHUs 2-2 and 2-3 were nearly identical and constant throughout the study. Formaldehyde concentrations in the zones served by AHUs 1-1 and 2-1 were mostly higher possibly indicating a localized source;

12

but, they were not associated with ventilation as the higher concentrations occurred at the higher airflow rates. Concentrations of acetaldehyde and hexanal with possible material sources (PC2) exhibited general trends of higher concentrations at lower flow rates in zones served by AHUs 1-1, 2-1 and 2-3. Concentrations of d-limonene with a probable air freshener and/or cleaning product source (PC5) were not strongly associated with ventilation in any zone. One relatively high outlying d-limonene value occurred on a single day in one location. The concentrations of d5 siloxane exhibited clear trends of higher concentrations at lower flow rates in zones served by AHUs 1-1 and 2-1. TMDP-MIB concentrations were elevated on three days in the zone served by AHU 2-2. All of the other TMPD-MIB values were low and relatively constant. This may have been due to the dependence of the TMPD-MIB emission rate on the bulk air concentration relative to the near surface gas-phase concentration in equilibrium with the sorbed surface concentration resulting in net re-emission from sinks at higher airflow rates.

These results illustrate that the efficacy of ventilation for controlling VOC concentrations can vary considerably depending upon the operation of the building, the pollutant sources and the physical and chemical processes affecting the pollutants. These factors combine to obscure a direct inverse relationship between concentration and ventilation for some VOCs.

In large buildings with multiple air handling zones, the degree of air mixing among zones may vary depending upon the operation of the ventilation system. For the purposes of this study, the building's air inlet dampers were manipulated to achieve periods of controlled, relatively constant ventilation. Consequently, normalized OA flow rates between several adjoining zones varied considerably during the study (Fig. 1), possibly affecting air mixing among these zones. In many cases, a large building's ventilation system does not operate at steady-state conditions. The effects attributable to air mixing may be amplified when, for example, variable air volume systems continually adjust the supply rates of cool or warm air to maintain desired indoor temperatures in various zones.

Many common VOCs are likely to have multiple sources of in a building. These sources, such as building materials and cosmetics, can have very different emission characteristics. For a

given source, there may be overriding temporal and spatial variations in generation rates that are unassociated with ventilation. As a primary example, concentrations of compounds that are solvent constituents of products used intermittently or sporadically in a building would not necessarily be expected to exhibit strong inverse relationships with ventilation. This was apparently the case for acetone, isopropanol and 2-butoxyethanol, which likely derived from the use of cleaning products/solutions. The sources of compounds that are strongly linked with occupancy also can vary spatially and temporally in association with the occupants' work and personal activities.

Physical and chemical processes affect the temporal pattern of pollutant net emission rates. Sink effects are indicated to be important for some VOCs based on these results. The sorption of VOCs onto interior surfaces in the building and their later release when bulk air concentrations decline directly links VOC emissions with ventilation to at least partially negate the benefit of increased ventilation. Since the building filters are in the mixed air plenums, any indoor VOCs sorbed onto the large surface areas of the filters also will desorb at higher rates with increased ventilation. For some common VOC source profiles and VOC/material combinations, this effect is predicted to be relatively large (Zhao *et al.*, 2002). In a study of a single large office building, the source strengths of C_{10}-C_{11} of isoparaffinic hydrocarbons emitted by wet-process photocopiers were quantified. The emission rates of these compounds measured over the weekend with very few occupants were about 20% of the weekday values likely due to re-emission from indoor surfaces (Hodgson *et al.*, 1991). In simulated room experiments, strongly sorbing VOCs emitted by a habitual intermittent source (environmental tobacco smoke) were lost quickly to surfaces and then released at slow rates over long periods (Singer *et al.*, in press). Indoor air chemistry involving the reaction of ozone with unsaturated compounds such as d-limonene is linked to ventilation since reactant losses are higher at low ventilation rate due to increased reaction times as shown by modeling and experiments (Weschler and Shields, 2000). All of these processes serve to reduce the general effectiveness of ventilation for controlling VOC sources.

Conclusions

Adequate ventilation is required to remove indoor-generated pollutants from buildings. However, differences in the concentrations of many of the abundant VOCs in the study building on seven days of sampling could not easily be predicted by the differences in ventilation rates on those days. A number of compounds likely had multiple sources with different emission characteristics. Temporal and spatial variations in cleaning products probably obscured the relationship between concentration and ventilation for some solvents. For other compounds, it is likely that net emission rates increased with ventilation due to their re-emission from sinks. These results emphasize the importance of employing source control measures to limit the concentrations of VOCs in office buildings. Source control should target the VOCs of most concern with respect to potential occupant health and comfort effects. Control procedures most readily can be applied to the products and materials that are used or consumed in buildings. They are less applicable to sources associated with personal activities such as the use of cosmetics, which were implicated as the possible source of several VOCs. Several potentially effective control procedures are use of exhaust ventilation for highly localized pollutant sources, use of low emitting materials to finish and furnish interiors, use of low-emitting cleaning products, and limited usage of products containing chemicals that are highly reactive with ozone.

Acknowledgements

References

Apte, M.G., Daisey, J.M., 1999. VOCs and "sick building syndrome": Application of a new statistical approach for SBS research to U.S. EPA BASE study data. In: Raw, G. (Ed.), Proceedings of the 8th Int. Conf. on Indoor Air Quality and Climate, Indoor Air 99. Construction Research Communications Ltd., London, UK, Vol. 1, pp. 117-122.

Apte, M.G., Erdmann, C.A., 2002. Associations of indoor carbon dioxide concentrations, VOCs, environmental susceptibilities with mucous membrane and lower respiratory sick building syndrome symptoms in the BASE study: Analyses of the 100 building dataset. Lawrence Berkeley Laboratory National Laboratory report LBNL-51570, Berkeley, CA.

ASTM, 1997a. Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology). Method D 5197-97, American Society for Testing and Materials, West Conshohocken, PA.

ASTM, 1997b. Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products. Guide D 5116-97, American Society for Testing and Materials, West Conshohocken, PA.

Daisey, J.M., Hodgson, A.T., Fisk, W.J., Mendell, M.J., Ten Brinke, J., 1994. Volatile organic compounds in twelve California office buildings: Classes, concentrations and sources. *Atmos. Environ*. 22, 3557-3562.

Eastman Chemical Co., 2003. Brands, Texanol, Applications. http://www.eastman.com/Brands/Texanol/listApplications.asp?pids=781. Web site accessed March 2003.

Edwards, R.D., Jurvelin, J., Koistinen, K., Saarela, K., Jantunen, M., 2001. VOC source identification from personal and residential indoor, outdoor and workplace microenvironment samples in EXPOLIS-Helsinki, Finland. *Atmos. Environ*. 35, 4829-4841.

Fenske, J.D., Paulson, S.E., 1999. Human breath emissions of VOCs. *J. Air Waste Manage. Assoc*. 49, 594-598.

Fisk, W.J., Price, P.N., Faulkner, D., Sullivan, D.P., Dibartolomeo, D.L., Federspiel, C.C., Liu, G., Lahiff, M., 2002. Worker performance and ventilation: Analysis of time-series data for a group of call-center workers. In Levin, H. (Ed.), Proceedings of the 9th Int. Conf. on Indoor Air Quality and Climate. Indoor Air 2002, Santa Cruz, CA, Vol. 1. pp. 790-795.

Girman, J.R., Hadwen, G.E., Burton, L.E., Womble, S.E., McCarthy, J.F., 1999. Individual volatile organic compound prevalence and concentration in 56 buildings of the building

survey and evaluation (BASE) study. In: Raw, G. (Ed.), Proceedings of the 8th Int. Conf. on Indoor Air Quality and Climate, Indoor Air 99. Construction Research Communications Ltd., London, UK, Vol., 2, pp. 460-465.

Hodgson, A.T., 1999. Common indoor sources of volatile organic compounds: Emission rates and techniques for reducing consumer exposures. Final report Contract No. 95-302, Calif. Environmental Protection Agency, Air Resources Board, Sacramento, CA.

Hodgson, A.T., Beal, D., McIlvaine, J.E.R., 2002. Sources of formaldehyde, other aldehydes and terpenes in a new manufactured house. *Indoor Air* 12, 235-242.

Hodgson, A.T., Daisey, J.M., Grot, R.A., 1991. Sources and source strengths of volatile organic compounds in a new office building. *J. Air Waste Manage. Assoc*. 41, 1461-1468.

Kelly, T.J., Smith, D.L., Satola, J., 1999. Emission rates of formaldehyde from materials and consumer products found in California homes. *Environ. Sci. Technol*. 33, 81-88.

Persily, A.K., 1997. Evaluating building IAQ and ventilation with indoor carbon dioxide. *ASHRAE Transactions*, Vol. 103, Pt. 2, pp. 193-204.

Rastogi, S.C., 1992. A survey of formaldehyde in shampoos and skin creams on the Danish market. *Contact Dermatitis* 27, 235-240.

Salthammer, T., 1997. Emission of volatile organic compounds from furniture coatings. *Indoor Air* 7, 189-197.

Seppänen, O.A., Fisk, W.J., Mendell, M.J., 1999. Association of ventilation rates and CO_2 concentrations with health and other responses in commercial and institutional buildings. *Indoor Air* 9, 226-252.

Shields, H.C., Fleischer, D.M., Weschler, C.J., 1996. Comparisons among VOCs measured in three types of U.S. commercial buildings with different occupant densities. *Indoor Air* 6, 2-17.

Singer, B.C., Hodgson, A.T., Nazaroff, W.W., In press. Gas-phase organics in environmental tobacco smoke: 2. Exposure-relevant emission factors and indirect exposures from habitual smoking. *Atmos. Environ*.

Ten Brinke, J., Selvin, S., Hodgson, A.T., Fisk, W.J., Mendell, M.J., Koshland, C.P., Daisey, J.M., 1998. Development of new volatile organic compound (VOC) exposure metrics and their relationship to "sick building syndrome" symptoms. *Indoor Air* 8, 140-152.

U.S. EPA, 1984. Method TO-1, Revision 1.0: Method For The Determination Of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS), Center for Environmental Research Information, Office of Research and Development, United States Environmental Protection Agency.

Weschler, C.J., Shields, H.C., 2000. The influence of ventilation on reactions among indoor pollutants: Modeling and experimental observations. *Indoor Air* 10, 92-100.

Zhao, D., Little, J.C., Hodgson, A.T., 2002. Modeling the reversible sink effect in response to transient contaminant sources. *Indoor Air* 12, 184-190.

Zhu J., Xu-Liang, C., Beauchamp, R., 2001. Determination of 2-butoxyethanol emissions from selected consumer products and its application in assessment of inhalation exposure associated with cleaning tasks. *Environ. Int*. 26, 589-597.

Table 1. Numbers of occupants and whole-building ventilation parameters on 7 sampling days.

Parameter	Units	Wk 2	Wk 3	Wk 6	Wk 7	Wk 8	Wk 11	Wk 13
Occupants[a]	Persons	217	211	215	243	226	217	273
Total OA[b] flow rate	$1,000 \ m^3 \ h^{-1}$	48.6	22.8	46.2	25.5	21.4	46.1	19.1
Area specific OA flow rate	$L \ s^{-1}/100 \ m^2$	292	137	277	153	128	277	115
Air exchange rate	h^{-1}	3.4	1.62	3.3	1.81	1.51	3.3	1.35

a. Average number of occupants from 8:00-15:00
b. Outdoor air

Table 2. Summary of indoor concentrations, outdoor concentrations and indoor/outdoor ratios of VOCs measured in 4 AHU zones on 7 sampling days (n = 28).

| Compound | Concentration (ppb) | | | | Indoor/Outdoor Ratio | |
| | Indoor | | Outdoor | | | |
	Geomean	Range	Geomean	Range	Geomean	Range
Ethanol	38	14.8-126	9.5	7.8-14.2	4.0	1.90-9.8
Isopropanol	44	18.7-250	9.7	9.1-10.1	4.6	1.86-27
1-Butanol	0.46	0.25-1.13	<0.11	<0.11-0.21	nm[a]	3.0->50
2-Ethyl-1-hexanol	0.41	0.19-1.07	0.07	<0.06-0.17	nm	1.46->50
2-Butoxyethanol	3.9	1.31-19.1	0.46	<0.07-1.46	8.3	1.53->50
Acetone	14.0	4.0-41	2.5	0.28-10.0	5.6	1.41-60
MIBK[b]	0.17	<0.08-2.2	<0.08	<0.08-0.15	nm	5.1->50
Formaldehyde	11.9	5.4-25	3.4	1.64-7.1	3.4	1.44-10.7
Acetaldehyde	3.0	1.4-7.1	1.68	0.81-3.9	1.79	0.91-3.2
Pentanal	0.48	0.21-0.87	0.21	0.15-0.31	2.3	0.88-5.2
Hexanal	1.15	0.61-2.2	0.29	0.21-0.36	4.0	1.88-10.1
Heptanal	0.27	0.14-0.54	0.14	0.10-0.18	1.90	0.77-4.7
Ethyl acetate	0.25	<0.09-2.5	<0.09	<0.09-0.17	nm	5.1->50
Butyl acetate	0.22	0.09-1.31	<0.07	<0.07-0.17	nm	1.73->50
TMPD-MIB[b]	0.17	<0.08-0.42	--	<0.08	nm	>50
Toluene	1.23	0.75-2.9	0.94	0.47-2.1	1.30	0.80-3.0
m/p-Xylene	0.50	0.31-1.12	0.40	0.24-0.78	1.25	0.80-2.2
Isoprene	0.76	<0.12-2.6	0.13	<0.12-0.44	nm	1.96->50
α-Pinene	0.38	0.09-0.87	<0.06	<0.06-0.11	nm	3.6->50
d-Limonene	0.83	0.22-4.9	--	<0.06	nm	>50
d5 Siloxane[b]	2.5	1.1-7.4	0.05	0.03-0.08	52	13.3->50

a. Not meaningful; concentration for majority of outdoor samples below lower limit of quantitation

b. MIBK = 4-Methyl-2-pentanone; TMDP-MIB = 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (combined isomers); d5 siloxane = Decamethylcyclopentasiloxane

Table 3. Whole-building emission factors of VOCs and CO_2 on 4 sampling days when building was operating at near steady-state conditions, and zonal average emission factors when AHU zones were operating near steady-state conditions (n = 21).

| | Emission Factor ($\mu g\ m^{-2}\ h^{-1}$) | | | | | |
| | Whole Building | | | | Zonal Average | |
Compound	Wk 2	Wk 6	Wk 7	Wk 13	Geomean	Range
Ethanol	290	480	280	380	320	153-780
Isopropanol	1,160	740	580	850	500	94-2,400
1-Butanol	20	8.7	5.8	4.9	8.1	3.0-31
2-Ethyl-1-hexanol	12.3	18.1	10.6	3.2	9.6	<1.43-22
2-Butoxyethanol	520	192	132	29	88	14.7-990
Acetone	260	136	183	187	144	29-410
MIBK[a]	4.5	3.8	2.2	2.4	4.2	1.60-70
Formaldehyde	121	111	58	25	54	20-220
Acetaldehyde	11.9	8.4	19.5	13.7	12.4	<8.7-30
Pentanal	2.4	3.2	8.6	6.8	4.6	<2.4-20
Hexanal	16.7	19.9	24	23	21	11.9-48
Heptanal	<3.5	3.1	6.3	3.7	3.3	<2.4-17.8
Ethyl acetate	6.8	3.3	12.2	2.9	6.2	0.67-25
Butyl acetate	8.7	5.8	1.98	3.0	5.4	<1.70-42
TMPD-MIB[a]	16.4	15.5	9.0	4.2	8.8	3.6-23
Toluene	<1.75	9.9	4.9	9.6	5.3	<1.23-17.4
Isoprene	8.8	11.2	13.1	18.5	11.7	5.5-28
α-Pinene	14.9	13.6	12.5	12.1	13.0	5.2-23
d-Limonene	56	26	55	22	31	12.6-150
d5 siloxane[a]	206	260	230	200	220	114-330
CO_2[b]	2.7	2.8	2.6	2.2	2.5	1.59-3.6

a. Defined in Table 2
b. Emission factor in $g\ m^{-2}\ h^{-1}$

Table 4. Loadings of the first five rotated principal components for analysis of emission factors of VOCs and CO_2. Compounds are sorted by loading from first to last principal components. Compound coefficients >0.5 are indicated in bold.

| Compound	Principal Component					Commun-ality
	1	2	3	4	5	
2-Ethyl-1-hexanol	**0.86**					0.75
TMPD-MIB*	**0.83**		0.34			0.95
Formaldehyde	**0.73**	-0.33	0.40			0.91
CO_2	**0.68**			0.37	0.34	0.81
d5 Siloxane*	**0.56**			**0.71**	0.48	0.80
MIBK*	0.37	**0.86**			-0.32	0.87
Butyl acetate	0.47	**0.82**		-0.38	-0.33	0.89
Acetaldehyde		**0.81**				0.72
Pentanal		**0.79**				0.87
Hexanal		**0.75**				0.78
Acetone			**0.92**			0.87
Isopropanol			**0.90**			0.88
2-Butoxyethanol	0.40		**0.84**			0.95
1-Butanol	0.44		**0.66**	-0.36		0.78
Toluene			-0.31	**0.84**		0.65
Isoprene				**0.71**		0.82
d-Limonene					**0.88**	0.87
Variance (%)	30	22	13	11	7	83 Total

*Defined in Table 2

Table 5. Whole building emission rates (ERs) and average per-occupant generation rates of isoprene, decamethylcyclopentasiloxane (d5 siloxane), and CO_2 on 4 sampling days when building was operating at near steady-state conditions. Occupants were assumed to be primary source of isoprene and d5 siloxane.

Parameter	Units	Wk 2	Wk 6	Wk 7	Wk 13
Isoprene ER	mg h^{-1}	41	52	61	86
Isoprene generation rate	mg h^{-1} occup^{-1}	0.188	0.24	0.25	0.31
d5 Siloxane ER	mg h^{-1}	950	1,210	1,060	940
d5 Siloxane generation rate	mg h^{-1} occup^{-1}	4.4	5.6	4.4	3.4
CO_2 ER	L s^{-1}	1.98	1.97	1.99	1.85
CO_2 generation rate	L s^{-1} occup^{-1}	0.0091	0.0092	0.0082	0.0068
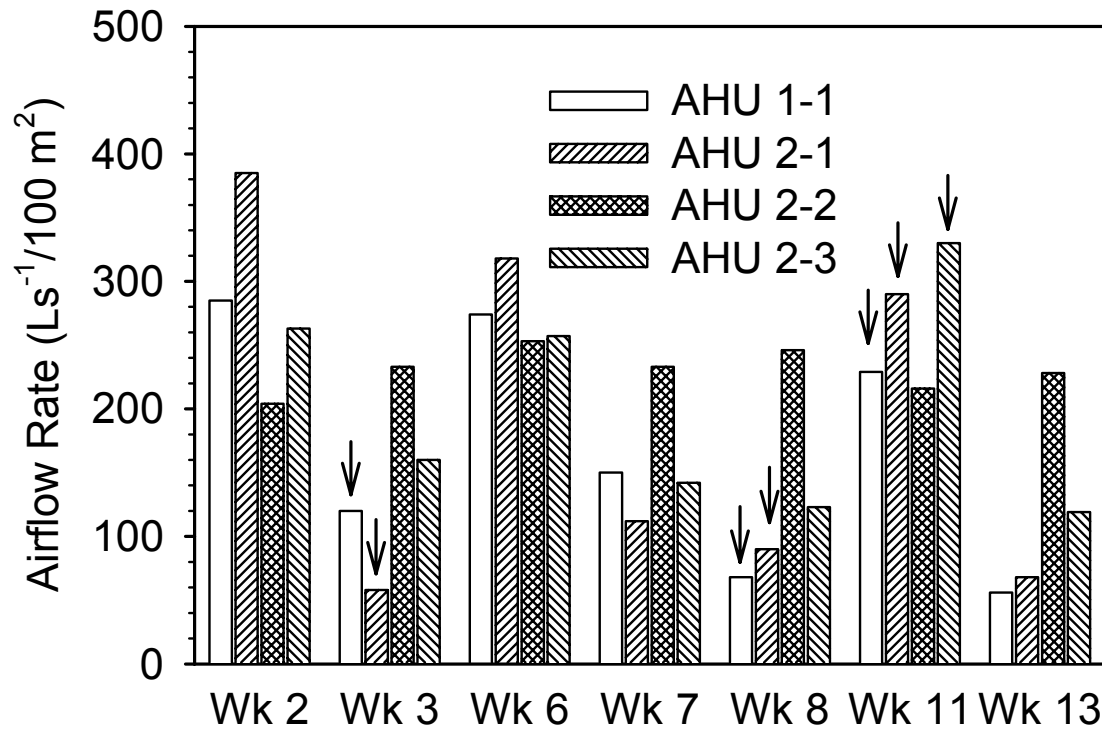
Figure 1. Normalized airflow rates in four AHUs on 7 sampling days. Arrows indicate non-steady state conditions.
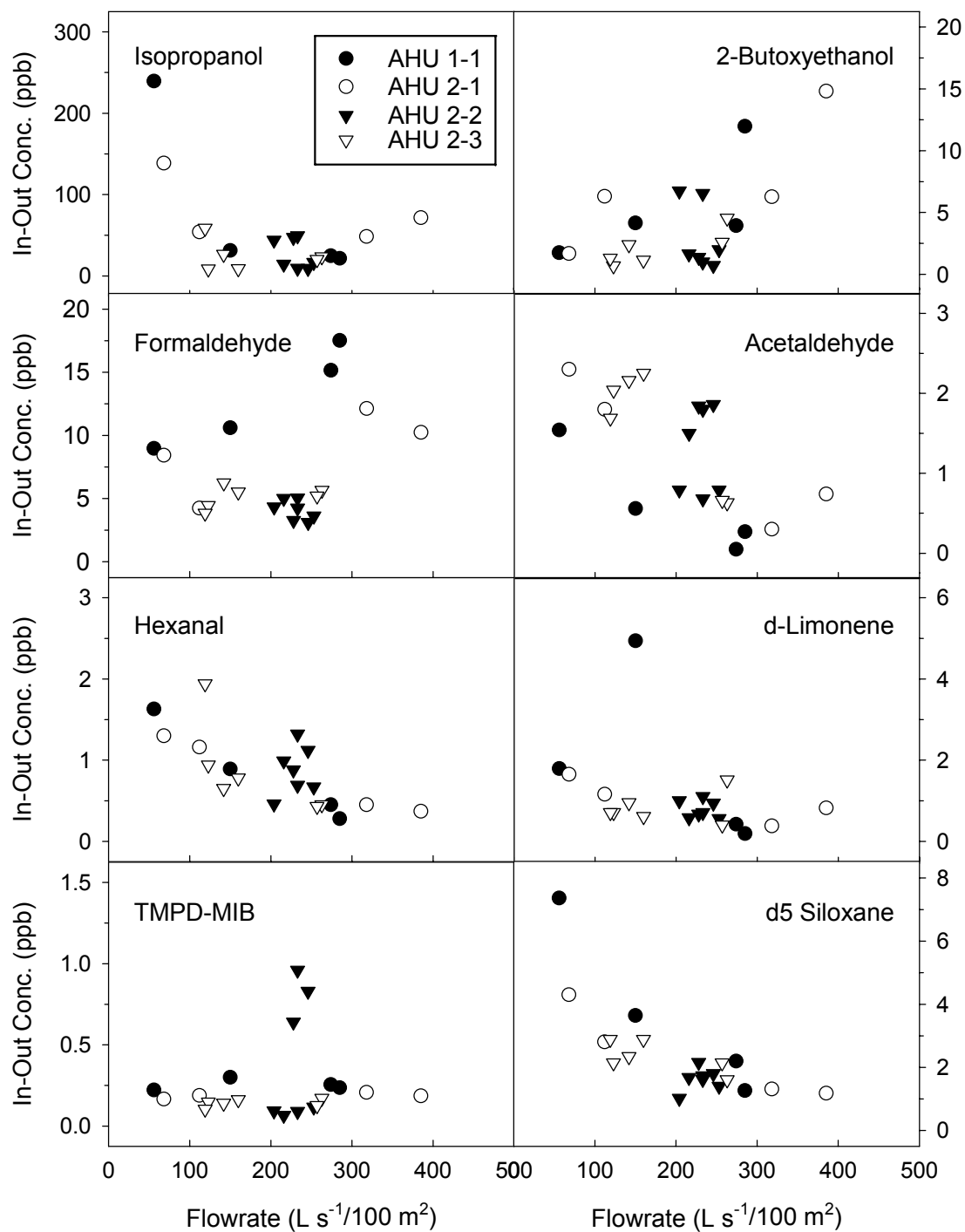
Figure 2. Indoor minus outdoor concentrations of 8 VOCs at near steady-state conditions in four AHUs on 7 sampling days versus normalized AHU airflow rates.